Chemosphere 95 (2014) 173–180

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Stability of solid-phase selenium species in fly ash after prolonged submersion in a natural river system

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HIGHLIGHTS

- XAS speciation of selenium in fly ash after long-term submersion in river.
- Selenium transformed into reduced organoselenium/selenium-sulfide species.
- Selenium was spatially correlated with Fe/Mn domains.

ARTICLE INFO

Article history:
Received 24 May 2012
Received in revised form 10 August 2013
Accepted 16 August 2013
Available online 3 October 2013

Keywords:
Fly ash
Selenium
XANES

ABSTRACT

Selenium (Se) chemistry can be very complex in the natural environment, exhibiting different valence states (−2, 0, +4, +6) representing multiple inorganic, methylated, or complexed forms. Since redox associated shifts among most of known Se species can occur at environmentally relevant conditions, it is important to identify these species in order to assess their potential toxicity to organisms. In June of 2009, researchers from the US Army Engineer Research & Development Center (ERDC) conducted investigations of the fly ash spilled 6 months previously into the Emory River at the TVA Kingston Fossil Plant, TN. Ash samples were collected on site from both the original ash pile (that did not move during the levee failure), from the spill zone (including the Emory River), and from the ash recovery ditch (ARD) containing ash removed during dredging cleanup operations. The purpose of this work was to determine the state of Se in the spilled fly ash and to assess its potential for transformation and resultant chemical stability from its prolonged submersion in the river and subsequent dredging. Sequential chemical extractions suggested that the river environment shifted Se distribution toward organic/sulfide species. Speciation studies by bulk XANES analysis on fly ash samples showed that a substantial portion of the Se in the original ash pile had transformed from inorganic selenite to a mixture of Se sulfide and reduced (organo)selenium (Se(-II)) species over the 6-month period. μ-XRF mapping data showed that significant trends in the co-location of Se domains with sulfur and ash heavy metals. Ten-d extended elutriate tests (EETs) that were bubbled continuously with atmospheric air to simulate worst-case oxidizing conditions during dredging showed no discernible change in the speciation of fly ash selenium. The enhanced stability of the organo- and sulfide-selenium species coincided with the mixture of the ash material with humic materials in the river, corresponding with notable shifts in the ash carbon- and nitrogen-functionality.

1. Introduction

The environmental fate of Se is closely linked to its redox state. Selenium is a highly versatile metalloid, able to assume multiple valence states (−2, 0, +4, +6) and multiple inorganic, methylated, or complexed forms. As oxyanions, selenite (Se(IV)) and selenate (Se(VI)) are mobile and relatively poorly adsorbed (compared to cationic metals) on natural solids (e.g., soils and sediments). For example, Hyun et al. (2006) measured Freundlich sorption coefficients on the order of 10^2–10^3 and 10^1–10^2 for selenite and selenate, respectively, in soils. One notable exception occurs in soils with definitive or concentrated iron-oxide domains. These domains have been shown to strongly adsorb oxidized Se, forming

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0045-6535/$ - see front matter Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.chemosphere.2013.08.061

either outer- or inner-sphere complexes with the oxyanions depending on Fe mineral type (Howard, 1977; Peak and Sparks, 2002). This strong association between Fe and inorganic Se typically drives the metal's environmental fate. The strong selenite–Fe-OH complex results in substantial shifts in the stability field distinguishing Se(IV) from Se(VI) oxidation states (Howard, 1977). Iron's control over inorganic Se governs abiotic transformations such as selenite reduction to elemental Se by suboxic Fe minerals such as green rust (Myeni et al., 1997), Fe(II,III) hydroxide, magnetite, siderite, and pyrite (Scheinost and Charlet, 2008, and references therein).

With the above exception, most Se transformations in the environment, however, are biologically mediated, and generally reductive in nature. Selenium is usually taken up from the environment in its mobile forms, selenite or selenate. Selenium's close competition with inorganic sulfur analogs for uptake by biota suggests the presence of multiple and competing transport pathways with contrasting Se and S selectivities (White et al., 2004). By and large, biological Se reduction serves as a means to either mitigate the toxic effects of the inorganic forms or provide energy to anaerobic microorganisms through dissimilatory processes (Sarret et al., 2005). Fortunately, selenium reduction is also thermodynamically favorable under the majority of natural conditions (Howard, 1977). Techniques such as inundating a contaminated soil with water (Frankenberger and Karlson, 1989) or "composting" drainage waters with rice straw (Zhang and Frankenberger, 2003) have been shown to immobilize Se through enzymatic reduction to the neutral elemental precipitate. Selenium is also reduced to organoselenium, which represents derivatives of thiol-bearing amino acids or alkylated sulfides. Common organoselenium compounds include selenomethionine (SeMet), selenocysteine (SeCys), and alkylated selenides. Although poorly mobile, organoselenium compounds also exhibit considerable toxicity (Oštádalová and Babicky, 1980; Nogueira et al., 2004) if consumed by organisms, either by causing cell damage through assimilation into protein synthesis (Montes-Bayon et al., 2002) or catalyzing the oxidation of biologically significant thiols like glutathione. Under this strategy, Se tolerance is typically associated with synthesis of nonprotein, methylated selenoamino acid derivatives, such as methylselenocysteine, -glutamyl-methylselenocysteine or selenocystathione (Brown and Shrift, 1981) through the reaction of a SeCys-methyl-transferase enzyme (Neuhierl et al., 1999), which serves to detoxify the compounds.

While selenium is commonly reduced by organisms in the environment, it is of interest as to what conditions are favorable for the oxidation of reduced compounds. Dowdle and Oremland (1998) showed that soil enriched with heterotrophic microbial cultures readily oxidized Se(0) to predominantly Se(IV), with a minor proportion of Se (VI). The authors concluded from this data that complete oxidation to selenate was limited by the sorption of selenite to the soil. But under a dredging scenario, it seems that the system oxidation would be linked to the exposure/mixture of atmospheric air. Lenz et al. (2008) presented detailed XANES evidence showing that anaerobic selenate-reducing biofilms contained a mixture of elemental, organic, and metal-bound selenium species. Out of the different species, organic selenium showed very limited resistance to oxidizing conditions, with these compounds quickly oxidized within 10 min of exposure to ambient air. Scott and Morgan (1996) showed evidence for a surface Mn(IV)–Se(IV) redox couple for oxidizing selenite to selenate at pH 4. However, this reaction was greatly reduced as pH was raised to 7 – conditions unfavorable for Mn(II) formation. The authors did not observe Se(IV) oxidation at pH 4 by dissolved oxygen in a birnessite-free system. Howard (1977) found that Fe oxide-bound Se(IV) was oxidized to Se(VI) under natural conditions, except in the presence of dissolved sulfides. Under the latter condition, the systems demonstrated a marked inability to oxidize Fe-bound selenite to selenate, in spite of extensive air bubbling (15 d) and pH adjustment to alkaline conditions (to induce selenite desorption from the Fe-oxides).

The distinct advantages of thermodynamically favorable selenium reduction via biological detoxification and dissimilatory processes strongly suggest such an endpoint would exist if fly ash was exposed to a biologically rich system, such as river sediments. If so, then the stability of the reduced selenium to oxidizing forces would greatly depend on the species of reduced selenium produced. For the current work, we present research investigating Se chemistry in coal fly ash following prolonged submersion in a natural river system. On 22nd of December 2008, a 60-ft pile of wet-stacked coal fly ash collapsed, rupturing retention walls, and spilling over 5 million cubic yards of fly ash into the Emory River and surrounding Swan Pond embankment. In June, 2009, ash and water samples collected at the site were characterized to determine the speciation of Se. The work reported here focuses predominantly on the solid phase analysis and characterization of Se in the ash and its stability against oxidation during dredging processes, after the ash's residence of nearly 6 months within the Emory River. This work can be viewed as a companion paper to Bednar et al. (2010), which focused on the solution phase composition and speciation of waters in contact with fly ash and sediment samples.

2. Materials and methods

2.1. Sample collection

For this work, composite fly ash samples were collected from the original source pile, the Emory River (EMR), and the ash recovery ditch (ARD) along the active dredge cell. Procedures for sample collection, handling, and storage are detailed in Bednar et al. (2010).

2.2. Characterization of site waters, ash, soils, and sediments

Total and dissolved metals in the site waters were determined using inductively coupled plasma atomic emission spectroscopy and mass spectrometry (ICP–AES and ICP–MS), following EPA Methods 6010C (ICP–AES) and 6020A (ICP–MS), using a Perkin Elmer Optima 5300DVs and Elan DRC-II, respectively.

Solid phase concentrations of metals in the fly ash and reference materials were determined by analysis of digestates. The solids were first dried, ground to pass a #40 ASTM sieve (Felt et al., 2008), and acid digested following USEPA method 3050B. The digestate was filtered through a #41 Whatman filter and diluted to 50 mL with 1% nitric acid. This digestate was further diluted with 1% nitric acid prior to ICP–AES and ICP–MS analysis as needed such that the analyte concentrations were within the instrument calibration range. Mercury was determined using cold vapor atomic fluorescence using a PS Analytical Atomic Fluorescence Instrument following USEPA method 7474. Dissolved organic and inorganic carbon was determined using a Shidmadzu TOC-V analyzer using a catalytic combustion technique.

Data from the above characterizations were further studied by multivariate statistical analysis in order to determine if (i) the chemical data was such that the fly ash samples were statistically distinguishable from the reference background samples and (ii) if any trends in the characterization data correlated concentrations of selenium with the other elemental constituents. For this, partial least squares (PLS) analysis was conducted on the log-transformed, mean-centered characterization data using the non-linear iterative partial least squares algorithm with full cross-validation.

A sequential extraction procedure modified from published methods (Tessier et al., 1979) was also performed on the fly ash materials as a companion analysis to the synchrotron based